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13. ABSTRACT (Maximum 200 Words) Inhibition of oxygen reduction is a very effective means for reducing corrosion of Al alloys and many other materials. The oxygen reduction reaction is quite complex, and very dependent on the existence of catalytic sites on the metallic surface. Recent projects on Al corrosion and inhibition have identified the importance of oxygen reduction, but have not elucidated the mechanism or the most effective means for its inhibition. The work proposed herein is not intended to comprehensively examine oxygen reduction, but it is directed toward identifying which aspects of an alloy promote O ₂ reduction. Once the nature of catalytic sites is understood, it should be possible to rationally select inhibitors that are effective for corrosion protection, as well as cost effective and environmentally more benign than chromate.				
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Final Report

July 1, 2006

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Award No.: F 49620-02-0321

Title: Mechanism and Inhibition of Oxygen Reduction on Light Weight Alloys

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Objectives:

- Identify cathodic sites on a range of Al alloys, including 7xxx alloys such as AA7075 and modern cleaner alloys, such as AA2524 and AA7055, using AFM, SKPFM, and microspectroscopy, including Raman and fluorescence imaging of pH, O₂ reduction products, and dissolved metal ions.
- Use the quartz crystal microbalance to separate the anodic and cathodic reactions on thin film analogs of intermetallic compounds as a function of potential and environment. This will provide detailed information on the reactivity of these compounds, including cathodic corrosion and dealloying.
- Evaluate cathodic inhibitors by observing the effects of inhibitor candidates on alloys in a galvanic split cell, and determining the nature of inhibitor interactions with alloys using microspectroscopy. Classes of inhibitor candidates include metal oxyanions such as vanadate and molybdate, organic thiols, and macrocyclic ligands which complex Fe, Mn, and Cu.

Report for September 2005 to March 2006:

The report below is condensed from a manuscript in preparation entitled ALUMINUM ALLOY CORROSION INHIBITION BY VANADATES,

Authors: M. Iannuzzi, T. Young and G. S. Frankel

Overview

Late in the project, Vanadium nuclear magnetic resonance (NMR) was found to be a key technique for characterizing vanadate solutions. In particular, it was possible to accurately determine the distribution of vanadium species as a function of pH, concentration, etc.

Furthermore, the inhibition of Al alloy corrosion by vanadates was considered in the context of oxygen reduction inhibition by various vanadium species.. Vanadium speciation is much more complicated than chromates, and critical to the inhibiting efficacy. Critical conditions for decavanadate polymerization from clear metavanadate solutions were investigated.

Decavanadate only formed when metavanadate was added to solutions of pH 3 or less. It was not possible to change the pH of a metavanadate solution without forming decavanadates, creating an orange colored solution. According to ⁵¹V NMR, monovanadates were present only in clear metavanadate solutions.; orange solutions always contained decavanadates and never contained monovanadates. Orange decavanadate solutions containing 0.5 M NaCl at pH 8.71 exhibited no significant inhibition of the oxygen reduction reaction and increasing decavanadate concentration was detrimental. In contrast, clear metavanadate solutions containing monovanadate exhibit strong inhibition of the oxygen reduction reaction, to a level similar to chromate. At a fixed pH, increased NaVO₃ concentration in clear metavanadate solutions increased inhibition efficiency.

Results

Determination of the minimum pH that triggers V₁₀ formation: the objective of these experiments was to determine the critical conditions (i.e. initial pH and final vanadate concentration) that cause decavanadate formation as evidenced by a change in color from clear to orange. The injection of the concentrated clear 150 mM NaVO₃ solution was made slowly and recorded with a digital camera. Figure 1 shows the pH_f as a function of pH₀. The color change associated with V₁₀ formation was only triggered for pH₀≤ 3, independent of final vanadate concentration. Interestingly, for 100 mM and 50 mM final vanadate concentrations, pH_f was

equal to 8.4 independent of pH_0 for $3 < pH_0 < 12$. For 5 mM total vanadate, pH_f was equal to 7.6 independent of pH_0 for $4 < pH_0 < 12$. In other words, to create vanadate solutions of concentration 5 mM or higher with pH less than 7.5, the vanadates must be mixed with solutions having pH less than 3-4. Since this pH range is above the pH for color change, a direct implication of these findings is the practical impossibility of adjusting the pH of clear NaVO_3 solutions without producing a change in color and speciation. Therefore, previous studies that investigated inhibition by vanadates at pH 7 actually used solutions containing decavanadate.. Exact speciation of these solutions will be addressed below. Once formed, however, orange decavanadate solutions can be adjusted to high pH without completely de-polymerizing the V_{10} formed during acidification. Therefore, it was possible to analyze and compare clear metavanadate and orange decavanadate solutions at a common pH only at high pH. Here solutions were adjusted to $pH = 8.71$, which corresponds to the as-dissolved pH of 100 mM NaVO_3 .

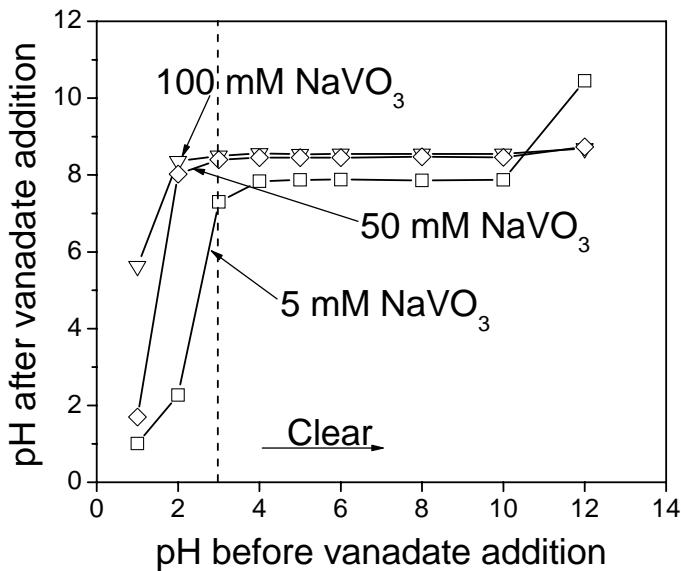


Figure 1. Final pH of solutions formed by mixing metavanadate with solutions of varying initial pH. The concentration refers to the final vanadate concentration after mixing.

The fact that a local environment with a $pH \leq 3$ triggers formation of decavanadates not only has direct implications in sample preparation procedures, but it might also impact coating schemes based on vanadates. The case of an epoxy coating containing a metavanadate pigment can be used as a simple example. If a scratch through the coating is exposed to an aggressive electrolyte, release of a vanadate species from the coating to the damaged area will occur. If the pH of the electrolyte is lower than 3, released metavanadates will polymerize to form decavanadates. In such a case, decavanadates will have to protect the exposed bare metal from further corrosion. On the other hand, if the pH of the aggressive electrolyte is greater than 4, metavanadates will be the species released and present in solution.

Nuclear Magnetic Resonance Spectroscopy (NMR): ^{51}V NMR was used to determine quantitatively the speciation of vanadate solutions. Decavanadates were prepared by first acidifying clear metavanadate solutions to pH 4 and then re-adjusting to pH 8.71. Since decavanadate solutions are not thermodynamically stable in these conditions, solutions were prepared immediately before NMR analysis.

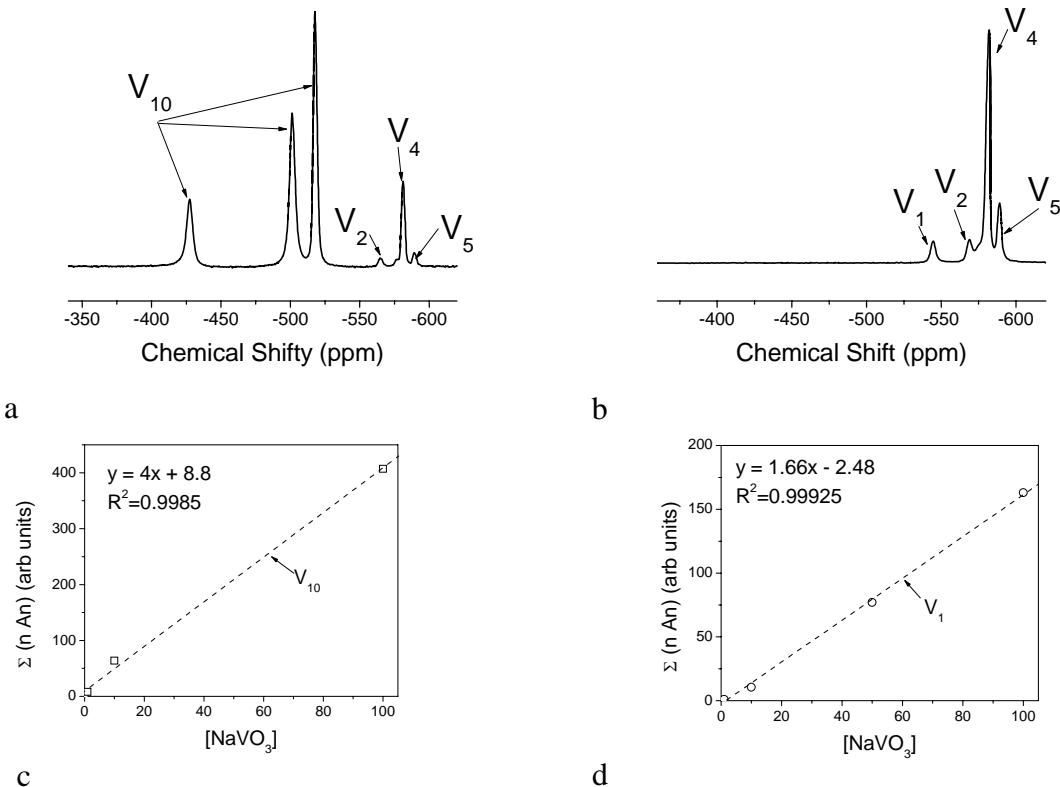


Figure 2. Assignment of ^{51}V NMR peaks and calibration. a) Typical ^{51}V NMR spectrum for an orange decavanadate solution b) typical ^{51}V NMR spectrum for a clear metavanadate solution c) calibration curve for orange decavanadate solutions d) calibration curve for clear metavanadate solutions.

Typical ^{51}V NMR spectra for a 100 mM decavanadate solution and a 100 mM metavanadate solution adjusted to pH 8.71 are shown in figures 2a and b. The peaks are labeled based on assignments reported in the literature.. NMR peaks are proportional to the species concentration. Summations of the peak areas of spectra such as those in figures 3 a and b from both decavanadate and metavanadate solutions of varying concentration are given in figures 3c and d, respectively. In both cases, the sum of n times the area under the peaks, where $n = 1,2,4,5$ or 10, linearly scaled with total vanadium concentration, thereby proving the validity of the peak assignment and providing a calibration of the method.

Figure 3 shows changes in speciation associated with pH adjustment. A typical ^{51}V NMR spectrum of a 100 mM clear metavanadate solution at pH 8.71 is shown in figure 2.4a. The oligomers present in such conditions are the monovanadate (V_1), the divanadate (V_2), the

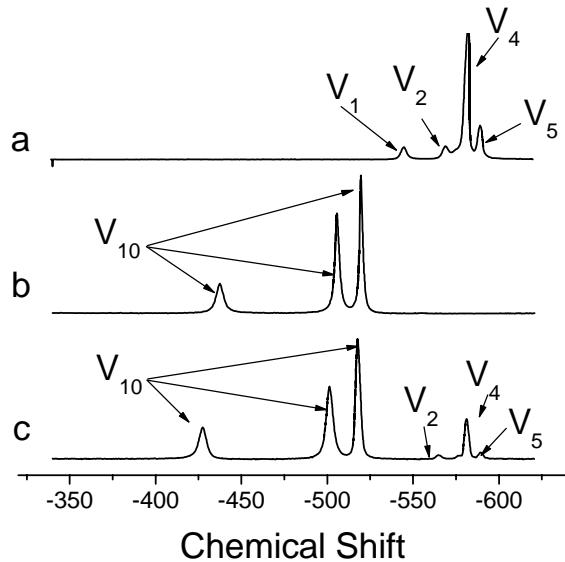


Figure 3. ^{51}V NMR spectra of 100 mM vanadate solution in different conditions: a) as-dissolved pH 8.71, b) acidified to pH 4, c) acidified and re-adjusted to pH 8.71.

tetravanadate (V_4) and the pentavanadate (V_5) as has been reported previously [1]. At low concentrations (1 to 5 mM NaVO_3) V_1 is the predominant species, whereas at higher concentrations, such as the case of figure 3a, the oligomers of higher molecular weight become predominant. When the clear metavanadate solutions are acidified to pH 4, all the metavanadates polymerize to form an orange decavanadate solution exclusively containing, within the detection limit of the instrument, signal from V_{10} oligomers (figure 4b). Increasing the pH of the decavanadate solutions produces the partial de-polymerization of V_{10} to give V_5 , V_4 , and V_2 (figure 3c). At low concentrations (1 to 5 mM NaVO_3), V_{10} is the predominant species and V_2 is the main metavanadate in these solutions with pH adjusted back to high values. As $[\text{NaVO}_3]$ increases, V_4 becomes the predominant metavanadate.

Comparison of figures 3a and b indicates that clear metavanadate solutions contain vanadate monomers whereas orange decavanadate solutions at pH 8.71 do not. In all of the orange solutions examined, V_{10} was always observed and V_1 was never observed. Figure 5 shows the concentration of V_1 species in clear metavanadate solutions and the concentration of V_{10} in orange decavanadate solutions as a function of the total vanadate concentration, all at pH = 8.71. The concentration of V_{10} linearly scales with total $[\text{NaVO}_3]$. However, the amount of V_1 present in clear metavanadate solutions seems to reach a saturation level of 6.5 mM.

Table 1 summarizes the chemical shifts, δ , observed for the different oligomers for both decavanadate and metavanadate solutions at pH 8.71. At a fixed pH the chemical shift of the different oligomers does not vary with incremental concentrations of NaVO_3 . Using chemical shift information, it is possible to determine the state of protonation of the oligomers. Within the experimental error of 0.5 ppm, the results are in good agreement with Heath et al. and Crans et al.. Nevertheless, chemical shifts are about 3 ppm more negative than commonly tabulated values. The small discrepancies are probably caused by different experimental conditions such as temperature, ionic strength and/or pH. For the clear solutions, the chemical shift of the monovanadates indicates that monoprotonated and diprotonated V_1 are present. The equilibrium

reaction for these species is shown in equation 2. Likewise, for both clear and orange solutions, the chemical shift for the divanadate species indicates that $\text{HV}_2\text{O}_7^{3-}$ and $\text{H}_2\text{V}_2\text{O}_7^{2-}$ are at equilibrium.. As hypothesized by Heath et al., the slightly more negative chemical shifts for both V_4 and V_5 may correspond to an equilibrium reaction between cyclic and linear oligomers. In addition, for the orange solutions, the position of the three V_{10} peaks seems to indicate that the decavanadate species at metastable-equilibrium are $\text{HV}_{10}\text{O}_{28}^{5-}$ and $\text{H}_2\text{V}_{10}\text{O}_{28}^{3-}$.

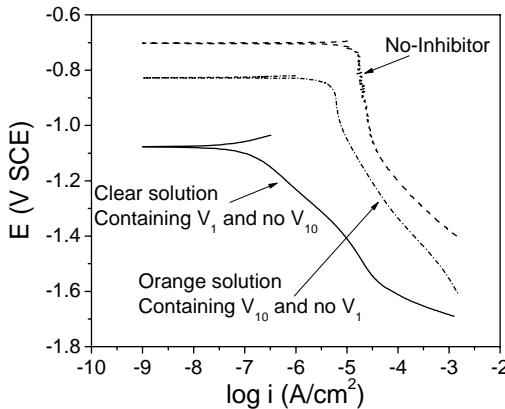
	Specie	Chemical Shift (ppm)
Clear	V_1	-545.55
	V_2	-569.62
	V_4	-581.13
	V_5	-589.34
Orange	V_2	-565.17
	V_4	-581.50
	V_5	-589.94
		-426.84
	V_{10}	-501.58
		-517.97

Table 1. Chemical shift for the different oligomers present in clear and orange solutions obtained by ^{51}V NMR.

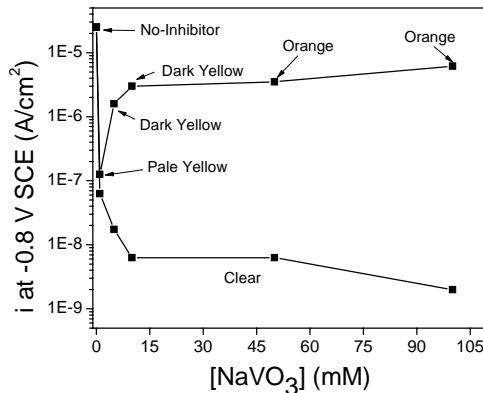
Inhibition by metavanadate and decavanadate solutions: The corrosion inhibiting effects of orange solutions containing decavanadate but no monovanadate and clear solutions containing metavanadates (V_1 through V_5) but no decavanadate were determined at the fixed pH of 8.71. These solutions will be referred to as orange decavanadate and clear metavanadate solutions, respectively, even though the former solutions also contain some metavanadates. Cathodic polarization curves of AA2024-T3 were measured in orange decavanadate and clear metavanadate pH 8.71 solutions containing 0.5 M NaCl and varying amounts of NaVO_3 . Figure 4a compares typical cathodic polarization curves for 100 mM NaVO_3 solutions. A cathodic polarization curve in 0.5 M NaCl with no vanadates is also shown for reference. In the absence of an inhibitor, the oxygen reduction reaction (ORR) is not impeded and a limiting current, i_L , of 25-30 $\mu\text{A}/\text{cm}^2$ is observed. The i_L obtained in Cu containing aluminum alloys is significantly larger than in pure Al or in Al alloys not alloyed with Cu. Although not completely understood, it is generally accepted that the presence of Cu contamination in the passive film on the matrix or on intermetallic particles increases conductivity of the oxide, making the diffusion of oxygen the rate limiting step. In pure Al, the alumina layer acts as an electric isolator causing electron transfer throughout the film to be extremely difficult. The ability to sustain a large cathodic current makes Al-Cu alloys very susceptible to localized corrosion. Therefore, if a corrosion inhibitor in the aggressive electrolyte controls the kinetics of oxygen reduction, a diminished corrosion rate is expected.

Figure 4a shows that orange decavanadate solutions do not reduce the kinetics of ORR significantly. For a 100 mM decavanadate solution, an average i_L of 8-15 $\mu\text{A}/\text{cm}^2$ is observed. The effects of NaVO_3 concentration are summarized in figure 4b. Comparison of the effects of vanadate on ORR kinetics is complicated by the different shapes of the polarization curves, especially at low potentials. The limiting current density values plotted in figure 4b were obtained by extrapolating the linear regions of the cathodic curves to the high potential of -800 mV SCE. This is an arbitrary definition and different approaches could have been taken.

However, it gives a fair representation of the inhibition efficacy. Higher vanadate concentrations resulted in larger limiting currents for the orange decavanadate solutions, supporting the concept that decavanadates are poor inhibitors of the ORR. The small amount of inhibition observed in decavanadate solutions is possibly a consequence of the presence of metavanadates such as V_2 . As the $NaVO_3$ concentration increases, the amounts of V_{10} and V_4 increase accordingly, lowering the V_2/V_4 ratio. It is hypothesized that adsorption of V_2 is somehow impeded by the presence of V_4 and V_{10} , which lowers the inhibition extent by allowing oxygen to adsorb freely on the local cathodes and then reduce.



a



b

Figure 4. Inhibition of ORR by vanadate solutions. a) Cathodic polarization curves of AA2024-T3 in 0.5M NaCl with no inhibitor, orange decavanadate, or clear metavanadate b) Effects of vanadate concentration on inhibition efficiency measured by calculating the cathodic current at $E = -800mV$ SCE.

In contrast to the orange decavanadate solutions, a significant difference in behavior is observed when analyzing clear metavanadate solutions. The kinetics of oxygen reduction were reduced by almost four orders of magnitude and no diffusion limiting region is observed, figure

4a. In addition, the threshold for hydrogen evolution is shifted toward more negative overpotentials. In further contrast to the orange decavanadate solutions, inhibition performance increased with increasing vanadate concentration, figure 4b. Since the orange decavanadate solutions contain no V_1 and the clear metavanadate solutions contain no V_{10} , these results suggest that decavanadates are detrimental or ineffective inhibitors and monovanadates provide the best inhibition. In this regard, the extent of inhibition imparted by monovanadates is similar to that reported for chromates and di-chromates in aqueous solutions. These data provide no insight on whether the monomers are adsorbed or reduced at the surface.. However, it is important to note that the efficacy of vanadate inhibition seems to reach a limiting value in the same range of $NaVO_3$ concentrations where the V_1 concentration reaches a limiting value.

A comparison of the long term performance of orange decavanadate and clear metavanadate solutions was carried out by analyzing polarization resistance values, R_P , extracted by LPT and by optical inspection after OCP exposure. Samples of AA2024-T3 were exposed to aerated pH 8.71 solutions containing 0.5 M NaCl with or without vanadates as indicated. Typical results are shown in figure 5. In the absence of inhibitor, R_P varied between 5 and 10 $k\Omega \text{ cm}^2$,

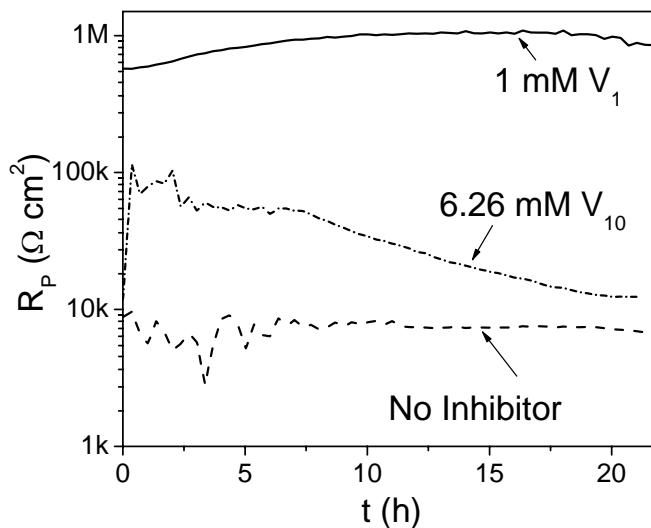


Figure 5. Polarization resistance of AA2024-T3 in 0.5M NaCl solutions containing no inhibitor, 1mM V_1 or 6.26 mM V_{10} .

and samples were severely pitted after the 24 h experiment. An orange decavanadate solution containing 6.26 mM V_{10} (present in a solution that was initially 100 mM $NaVO_3$) exhibited R_P values that fluctuated between 50 and 300 $k\Omega \text{ cm}^2$ initially. However, after about 5 h, R_P decreased with time to 10-30 $k\Omega \text{ cm}^2$. In contrast, in a clear metavanadate solution containing 1 mM V_1 (present in a solution that was initially 1mM $NaVO_3$), significantly higher R_P values were observed. Polarization resistance typically varied between 300-1100 $k\Omega \text{ cm}^2$ and was virtually independent of $NaVO_3$ concentration above 1mM. The low corrosion rate was sustained during the 24 h of exposure. Samples exposed at OCP to orange decavanadate solutions containing NaCl rapidly developed pits that could be observed easily with the unaided eye. Figure 6a is an optical micrograph of an AA2024-T3 after 14 days in an orange decavanadate + chloride solution with initial total vanadate concentration of 10 mM. Very large pits at the surface are evident. In contrast, only small pits were observed after exposure to clear

metavanadate + chloride solutions, figure 6b. Interestingly, in both cases, pits were always covered by a corrosion product that was enriched in vanadium as shown by EDS (figure 6c).

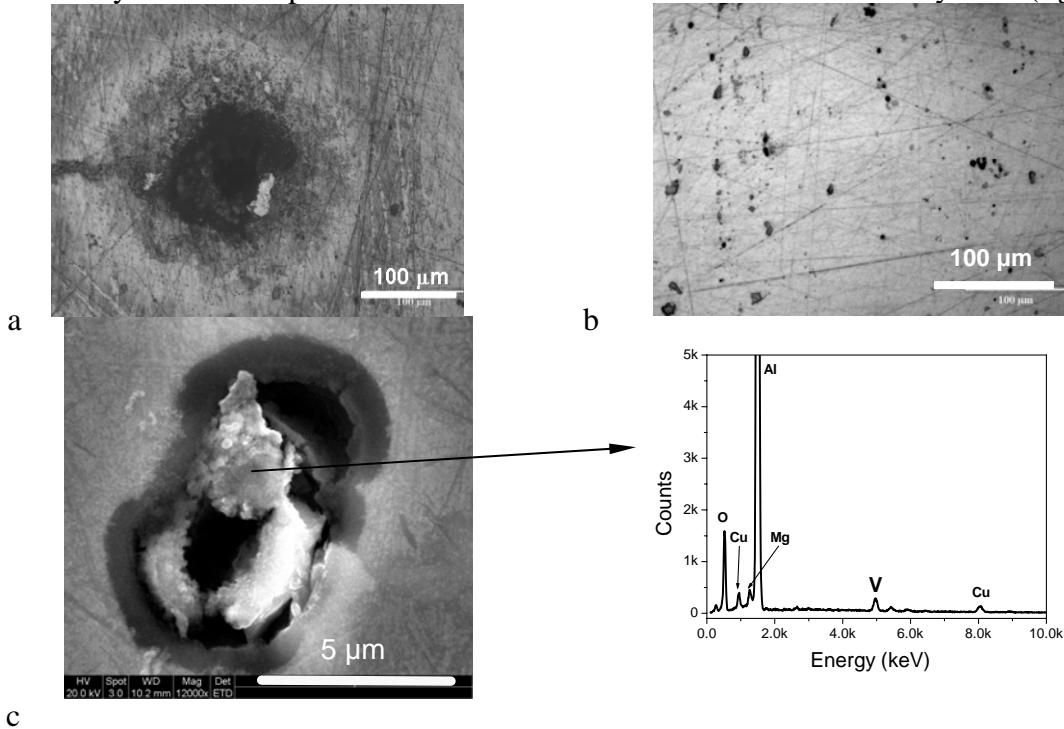


Figure 6. Optical micrographs of AA2024-T3 after 14 days of exposure to aerated 0.5 M NaCl containing a) V_1 and b) V_{10} . c) Secondary electron image of a small pit nucleated after 14 days exposure to V_1 , and EDS analysis of the corrosion products showing enrichment in vanadium.

Importance to Aircraft corrosion protection

These findings should directly impact the development of new coating systems based on vanadates. To date, most of the work with vanadium compounds was focused on hosting decavanadates in hydrotalcite pigments or in conversion coatings. Since monovanadate appears to be the actual corrosion inhibitor of the system, any coating scheme based on vanadium should release V_1 . The electrolyte developed in atmospheric exposure of aircrafts is thought to be basic, which would impede the formation of decavanadate. Special care should also be taken during coating formulation. Since $pHs < 3$ triggers decavanadate formation, the pH of the coating bath has to remain above that critical level. The main problem of $NaVO_3$ as pigment is its relatively large solubility, which would end up producing blistering after water uptake. However, Smith et al. and Nazarov et al. produced a variety of vanadate pigments with a lower solubility than $NaVO_3$, by simply reacting $NaVO_3$ with different metallic-chlorides such as $MgCl_2$ and $SrCl_2$. This suggests that it could be possible to have control over the release kinetics.

Finally, it is unclear what would happen inside an acidic crevice. However, the absence of crevice attack under masked regions during long term exposure seems to indicate that the blockage of the local cathodes by monovanadates diminishes any possible anodic dissolution, including crevice corrosion. Nevertheless, a more detailed investigation is still required.

Conclusions:

Speciation of vanadate solutions with varying concentrations and pH was studied by ^{51}V NMR spectroscopy and the effects of corrosion inhibition for AA2024-T3 were investigated. The following conclusions can be obtained:

1. Decavanadate only formed when metavanadate was added to solutions of pH 3 or less. The final pH after vanadate addition was independent of the initial pH for initial pH of 3 or greater. Therefore, it is impossible to change the pH of a metavanadate solution without forming decavanadates.
2. Acidification of clear metavanadate solutions to pH 4 or lower polymerizes all the oligomers to form V_{10} . Readjusting the pH to 8.71 produces a partial de-polymerization of V_{10} to form V_2 , V_4 and V_5 . Orange solutions always contained decavanadates and never contained monovanadates
3. Orange decavanadate solutions containing 0.5 M NaCl exhibited no significant inhibition of the oxygen reduction reaction and increasing decavanadate concentration was detrimental. Aging of the metastable decavanadate solutions for up to 10 days did not improve protection.
4. Clear metavanadate solutions containing monovanadate exhibit strong inhibition of the oxygen reduction reaction, to a level similar to chromate. At a fixed pH, increased NaVO_3 concentration in clear metavanadate solutions increased inhibition efficiency.
5. Since the orange decavanadate solutions contain no V_1 and the clear metavanadate solutions contain no V_{10} , these results suggest that decavanadates are detrimental or ineffective inhibitors and monovanadates provide the best inhibition.
6. At higher pHs V_1 and V_2 become the predominant species but improvement in inhibition was found.
7. A coating system based on vanadates should be able to release monovanadates. The formation of decavanadates during coating formulation should be avoided.

Titles of additional papers anticipated from the project:

1. MECHANISMS OF INHIBITION OF AA2024-T3 CORROSION BY DECAVANADATES AND METAVANADATES IN AQUEOUS SOLUTIONS CONTAINING CHLORIDE IONS.
2. INHIBITION OF AA2024 CORROSION BY CLEAR METAVANADATES AND ORANGE DECAVANADATE SOLUTIONS: AN IN SITU AFM SCRATCHING INVESTIGATION